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(54) **Ethylene oxide catalyst, process for its production and use.**

(57) This invention relates to an ethylene oxide catalyst having improved selectivity stability which catalyst comprises silver, a promoting amount of alkali metal, a promoting amount of rare earth, a promoting amount of rhenium and, optionally, a promoting amount of rhenium co-promoter selected from sulphur, molybdenum, tungsten, chromium and mixtures thereof, supported on a porous refractory support.

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The invention relates to silver-containing catalysts suitable for the preparation of ethylene oxide and to the use of the catalysts for the preparation of ethylene oxide.

Catalysts for the production of ethylene oxide from ethylene and molecular oxygen are generally supported silver catalysts. Such catalysts are typically promoted with alkali metals. The use of small amounts of the alkali metals potassium, rubidium and cesium were noted as useful promoters in supported silver catalysts in U.S. Patent No. 3,962,136 and U.S. Patent No. 4,010,115. The use of other co-promoters, such as rhenium, or rhenium along with sulphur, molybdenum, tungsten and chromium is disclosed in U.S. Patent No. 4,766,105 and U.S. Patent No. 4,808,738. U.S. Patent No. 4,908,343 discloses a supported silver catalyst containing a mixture of a cesium salt and one or more alkali metal and alkaline earth metal salts.

U.S. Patent No. 4,257,976 discloses a catalyst combination of reduced silver, a carbonate of a rare earth metal and yttrium, a salt of an alkali or alkaline earth metal and a catalyst carrier.

None of these references disclose the use of a promoting amount of rare earth which is present on a silver-based, alkali metal/rhenium-doped supported catalyst.

The present invention relates to a catalyst for the production of ethylene oxide from ethylene and molecular oxygen in the vapour phase which catalyst comprises a catalytically effective amount of silver, a promoting amount of alkali metal, a promoting amount of a rare earth metal compound, a promoting amount of rhenium and optionally, a rhenium co-promoter selected from sulphur, molybdenum, tungsten, chromium and mixtures thereof supported on a porous, refractory support.

It has been found that catalysts containing a promoting amount of rare earth compound have higher selectivity stabilities than those obtained with catalysts containing no rare earth compound.

Generally, in the vapour phase reaction of ethylene with oxygen to produce ethylene oxide, the ethylene is present in at least a double amount (on a molar basis) compared with oxygen, but often much higher. Therefore, the conversion is calculated according to the mole percentage of oxygen which has been consumed in the reaction to form ethylene oxide and any oxygenated by-products. The oxygen conversion is dependent on the reaction temperature, and the reaction temperature is a measure of the activity of the catalyst employed. The catalyst activity value T40 indicates the temperature at 40 mole percent oxygen conversion in the reactor and the value T is expressed in °C. The catalyst selectivity (to ethylene oxide) indicates the molar amount of ethylene oxide in the reaction product compared with the total molar amount of ethylene converted. The selectivity is indicated as S40, which means the selectivity at 40 mole percent oxygen conversion. The selectivity of silver-based ethylene oxide catalysts can and will decrease over a period of time of usage. Therefore, from an economic and practical standpoint, it is not only the initial selectivity of a catalyst which is important, but also the rate at which the selectivity declines. In fact, significant improvement in lowering the decline rate of a catalyst can prove more economically attractive than a high initial selectivity. Thus, the rate at which a catalyst loses selectivity is a predominant factor influencing the efficiency of any particular catalyst, and lowering this decline rate can lead to significant savings in terms of minimizing waste of the ethylene starting material. As used herein, "selectivity" is used to refer to the selectivity of ethylene oxide catalysts when measured at a given constant oxygen conversion level of 40% at a gas hourly space velocity of approximately 3300 and when measured after the catalyst has been placed on stream for at least several days.

In general, the catalysts of the present invention are prepared by impregnating porous refractory supports with silver ions or compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to cause deposition on the support of from 1 to 30 percent by weight, based on the weight of the total catalyst, of silver. The impregnated support is then separated from the solution and the deposited silver compound is reduced to metallic silver. Also deposited on the support either prior to, coincidentally with, or subsequent to the deposition of the silver will be suitable ions, or compound(s) and/or salt(s) of alkali metal dissolved in a suitable solvent, suitable rare earth compound(s), complex(es) and/or salt(s) dissolved in an appropriate solvent and suitable rhenium ions or compound(s), complex(es) and/or salt(s) dissolved in an appropriate solvent. In a preferred embodiment, suitable ions or salt(s), complex(es) and/or compound(s) of sulphur, molybdenum, tungsten and/or chromium dissolved in an appropriate solvent will be deposited on the carrier either prior to, coincidentally with, or subsequent to the deposition of the silver and/or alkali metal and/or rare earth and/or rhenium.

The carrier or support employed in these catalysts in its broadest aspects can be any of the large number of conventional, porous refractory catalyst carriers or support materials which are considered relatively inert in the presence of ethylene oxidation feeds, products and reaction conditions. Such conventional materials are known. They may be of natural or synthetic origin and preferably of a macroporous structure, i.e., a structure having a surface area from 0.01 to 10 m<sup>2</sup>/g and preferably below 3 m<sup>2</sup>/g. Particularly suitable supports are those of aluminous composition. Examples of supports which have been used as supports for different catalysts and which could be used as supports for ethylene oxide

catalysts are the aluminium oxides (including the materials sold under the trade name "Alundum"), charcoal, pumice, magnesia, zirconia, keiselguhr, fuller's earth, silicon carbide, porous agglomerates comprising silica and/or silicon carbide, silica, magnesia, selected clays, artificial and natural zeolites and ceramics. Refractory supports especially useful in the preparation of catalysts in accordance with this invention comprise the aluminous materials, in particular those comprising alpha alumina. In the case of alpha alumina-containing supports, preference is given to those having a specific surface area as measured by the B.E.T. method of from 0.03 m<sup>2</sup>/g to 10 m<sup>2</sup>/g, preferably from 0.05 m<sup>2</sup>/g to 5 m<sup>2</sup>/g, more preferably from 0.1 m<sup>2</sup>/g to 3 m<sup>2</sup>/g, and a water pore volume as measured by conventional water absorption techniques of from 0.1 to 0.75 cc/g by volume. The B.E.T. method for determining specific surface area is described in detail in Brunauer, S., Emmet, P. Y. and Teller, E., *J. Am. Chem. Soc.*, 60, 309-16 (1938).

Certain types of alpha alumina containing supports are particularly preferred. These alpha alumina supports have relatively uniform pore diameters and are more fully characterized by having B.E.T. specific surface areas of from 0.1 m<sup>2</sup>/g to 3 m<sup>2</sup>/g, preferably from 0.1 m<sup>2</sup>/g to 2 m<sup>2</sup>/g, and water pore volumes of from 0.10 ml/g to 0.55 ml/g. Typical properties of some supports found particularly useful in the present invention are presented in Table I. Suitable manufacturers of carriers comparable to those in Table I include Norton Company and United Catalysts, Inc. (UCI).

TABLE I

Carrier	A	B	C	D	E	F
B.E.T. Surface Area, m <sup>2</sup> /g(a)	0.21	0.42	0.51	0.48	0.57	2.06
Water Pore Volume, cc/g	0.26	0.36	0.38	0.49	0.44	0.65
Crush Strength, FPGS, lbs(b)	100%	97%	21	14	15	No Data
	20	15				
	lbs					
Total Pore Volume, Hg, cc/g(c)	1.26	0.42	0.40	0.46	0.42	0.65
Average Pore Diameter, Hg, Å(c)	620	560		550	770	1000
Median Pore Diameter, Hg, microns(c,e)	3.7	2.7	3.5	3.4	2.4	2.5
Percent Pore Volume in Pores Greater Than 350Å(c)	90.0%	88.5%	93.0%	89.1%	91.5%	94.1%

TABLE I (cont'd)

Carrier	A	B	C	D	E	F
Percent Pore Volume in Pores Greater Than 1 Micron(c)	87.0%	82.5%	77.0%	82.3%	83.5%	61.0%
% Wt. Alpha Alumina	99.5	98	98.8	98.5	98	70-75
Water Leachable Na, ppmw	12	53	69	24	18	No Data
Acid-Leachable Na, ppmw	40	96	188	51	45	No Data
Water Leachable K, ppmw	5	22	32	22	10	No Data
Acid-Leachable Fe, ppmw	2	5	No Data	1	5	No Data
% Wt. SiO <sub>2</sub>	.5	2	0.1	15	2	25-30

(a) Method of Brunauer, Emmet and Teller, loc. cit.

(b) Flat Plate Crush Strength, single pellet.

(c) Determined by mercury intrusion to 379,225 kPa using Micromeritics Autopore 9200 or 9210 (130° Contact angle, 0.473 N/m surface tension of Hg).

(e) Median pore diameter represents the pore diameter wherein 50% of the total pore volume is found in pores having less than (or greater than) the median pore diameter.

Of the carriers listed in TABLE I, B and C are preferred because they provide catalysts which have high initial selectivities.

Particular supports having differing properties such as surface area and pore volume may be selected in order to provide particular catalytic properties.

The preferred method is to deposit silver, alkali metal, rare earth, rhenium and rhenium co-promoter simultaneously on the support, that is, in a single impregnation step, although it is believed that the individual or concurrent deposition of the alkali metal, rare earth, rhenium and rhenium co-promoter, if present, prior to and/or subsequent to the deposition of the silver would also produce suitable catalysts.

As used herein, the term "promoting amount" of a certain component of a catalyst refers to an amount of that component which works effectively to provide an improvement in one or more of the catalytic properties of that catalyst when compared to a catalyst not containing said component. Examples of catalytic properties include, inter alia, operability (resistance to runaway), selectivity, activity, conversion, stability and yield.

The particular combination of silver, support, rare earth promoter, alkali metal promoter, rhenium promoter and optionally, rhenium co-promoter of the instant invention will provide an improvement in one or more catalytic properties over the same combination of silver, support, alkali metal promoter, rhenium

promoter and optionally, rhenium co-promoter and no rare earth promoter.

Promoting amounts of alkali metal or mixtures thereof, and or rare earth metals, are deposited on a porous support using a suitable solution. Although alkali metals and rare earth metals exist in a pure metallic state, they are not suitable for use in that form. They are used as ions or compounds dissolved in a suitable solvent for impregnation purposes. The carrier is impregnated with a solution of alkali metal promoter and rare earth metal ions, salt(s) and/or compound(s) before, during or after impregnation of the silver ions or salt(s), complex(es), and/or compound(s) has taken place. An alkali metal promoter and/or a rare earth metal may even be deposited on the carrier after reduction to metallic silver has taken place. The promoting amount of alkali metal and rare earth metal utilized will depend on several variables, such as, for example, the surface area and pore structure and surface chemical properties of the carrier used, and the contents of the other components of the catalyst composition.

The amount of alkali metal promoter deposited upon the support or present on the catalyst generally lies between 10 and 3000, preferably between 15 and 2000, more preferably between 20 and 1500 and most preferably between 50 and 1000 parts per million by weight of the total catalyst.

The amount of rare earth promoter deposited upon the support or present on the catalyst generally lies between 10 and 1000, preferably between 15 and 500 and most preferably between 30 and 250 parts per million by weight of the total catalyst.

The alkali metal promoters and the rare earth metals are present on the catalysts in the form of cations (ions) or compounds of complexes or surface compounds or surface complexes rather than as the extremely active free metals. For purposes of convenience however, the amount of alkali metal and rare earth metal deposited on the support or present on the catalyst is expressed as the metal. Without intending to limit the scope of the invention, it is believed that the alkali metal compounds and the rare earth metal compounds are oxidic compounds. More particularly, it is believed that the alkali metal compounds and the rare earth metal compounds are probably in the form of mixed surface oxides or double surface oxides or complex surface oxides with the aluminium of the support and/or the silver of the catalyst, possibly in combination with species contained in or formed from the reaction mixture, such as, for example, chlorides or carbonates or residual species from the impregnating solution(s).

As used herein, the term "alkali metal" and cognates thereof refers to the alkali metals selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and mixtures thereof. The term "mixtures of alkali metals" or cognates of these terms refers to the use of two or more of the alkali metals, as appropriate, to provide a promoting effect. A preferred alkali metal promoter is cesium. A particularly preferred mixture of alkali metals is cesium plus at least one additional alkali metal. The additional alkali metal is preferably selected from sodium, lithium and mixtures thereof, with lithium being preferred.

The most preferred promoter is cesium plus lithium, preferably applied in an aqueous solution having cesium nitrate or cesium hydroxide dissolved therein.

It should be understood that the amounts of alkali metal promoters on the catalysts are not necessarily the total amounts of these metals present in the catalyst. Rather, they are the amounts of alkali metal promoters which are extractable. These amounts do not include amounts of alkali metals which are locked into the support, for example, by calcining, or are not extractable in a suitable solvent such as water or lower alkanol or amine or mixtures thereof and do not provide a promoting effect. It is also understood that a source of the alkali metal promoter ions, salts and/or compounds used to promote the catalyst may be the carrier. That is, the carrier may contain extractable amounts of alkali metal that can be extracted with a suitable solvent, such as water or lower alkanol.

As used herein, the terms "rare earth metal" and "rare earth" refer to the rare earth metals or elements having atomic numbers 58 through 71 in the Periodic Table of the Elements i.e., cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. As used herein, the term "mixtures of rare earth metals" refers to the use of two or more of the rare earth metals.

In a preferred embodiment, the rare earth metal is one or more of the earth metals selected from the group consisting of cerium, neodymium, samarium, gadolinium, dysprosium, erbium, ytterbium, and mixtures thereof, with cerium, neodymium, gadolinium, ytterbium, and mixtures thereof being particularly preferred. Particularly preferred rare earth promoters are gadolinium, cerium and ytterbium.

The carrier is also impregnated with rhenium ions, salt(s), compound(s), and/or complex(es). This may be done before, at the same time, or later than one or more of the other components of the catalyst compositions. Preferably, rhenium, rare earth, alkali metal, optional rhenium co-promoter and silver are in the same impregnating solution, although it is believed that their presence in different solutions will still provide suitable catalysts. The preferred amount of rhenium, calculated as the metal, deposited on or present on the carrier or catalyst ranges from 0.1 to 10, more preferably from 0.2 to 5 micromoles per gram

of total catalyst, or, alternatively stated, from 19 to 1860, preferably from 37 to 930 parts per million by weight of total catalyst. For purposes of convenience, the amount of rhenium present on the catalyst is expressed as the metal, irrespective of the form in which it is present.

The rhenium compounds used in the preparation of the instant catalysts are rhenium compounds that can be solubilized in an appropriate solvent. Preferably, the solvent is a water-containing solvent. More preferably, the solvent is the same solvent used to deposit the silver and the alkali metal promoter. Examples of suitable rhenium compounds include the rhenium salts such as rhenium halides, the rhenium oxyhalides, the rhenates, the perrhenates, the oxides and the acids of rhenium. A preferred compound for use in the impregnation solution is the perrhenate, preferably ammonium perrhenate. However, the alkali metal perrhenates, alkaline earth metal perrhenates, silver perrhenates, other perrhenates and rhenium heptoxide can also be suitably utilized. Rhenium heptoxide,  $\text{Re}_2\text{O}_7$ , when dissolved in water, hydrolyzes to perrhenic acid,  $\text{HReO}_4$ , or hydrogen perrhenate. Thus, for purposes of this specification, rhenium heptoxide can be considered to be a perrhenate, i.e.,  $\text{ReO}_4$ . It is also understood that there are many rhenium compounds that are not soluble per se in water. However, these compounds can be solubilized by utilizing various acids, bases, peroxides, alcohols, and the like. After solubilization, these compounds could be used, for example, with an appropriate amount of water or other suitable solvent to impregnate the carriers. Of course, it is also understood that upon solubilization of many of these compounds, the original compound no longer exists after solubilization. For example, rhenium metal is not soluble in water. However, it is soluble in concentrated nitric acid as well as in hydrogen peroxide solution. Thus, by using an appropriate reactive solvent, one could use rhenium metal to prepare a solubilized rhenium-containing impregnating solution. In a preferred embodiment of the instant invention, the rhenium present on the catalyst is present in a form that is extractable in a dilute aqueous base solution.

U.S. Patent No. 4,766,105, mentioned above, discloses rhenium co-promoters which, when added to an alkali metal/rhenium doped supported silver catalyst, improve the initial selectivity of those catalysts. While suitable catalysts can be prepared in the absence of a rhenium co-promoter, it is preferable that the catalyst in the present invention contain a rhenium co-promoter. The co-promoter is selected from the group consisting of sulphur, molybdenum, tungsten, chromium and mixtures thereof, preferably a compound of sulphur, molybdenum, tungsten, chromium and mixtures thereof. The exact form of the co-promoter on the catalyst is not known. The co-promoter, it is believed, is not present on the catalyst in the elemental form since the co-promoter is applied to catalyst in the form of ions, salts, compounds and/or complexes and the reducing conditions generally used to reduce the silver to metallic silver are not usually sufficient to reduce the sulphur, molybdenum, tungsten or chromium to the elemental form. It is believed that the co-promoter deposited on the support or present on the catalyst is in the compound form, and probably in the form of an oxygen-containing or oxidic compound. In a presently preferred embodiment, the co-promoter is applied to the catalyst in the oxyanionic form, i.e. in the form of an anion, or negative ion which contains oxygen. Examples of anions of sulphur that can be suitably applied include sulfate, sulfite, bisulfite, bisulfate, sulfonate, persulfate, thiosulfate, dithionate, etc. Preferred compounds to be applied are ammonium sulfate and the alkali metal sulfates. Examples of anions of molybdenum, tungsten and chromium that can be suitably applied include molybdate, dimolybdate, paramolybdate, other iso- and hetero-polymolybdates, etc.; tungstate, paratungstate, metatungstate, other iso- and hetero-polytungstates, etc.; and chromate, dichromate, chromite, halochromate, etc. Preferred are sulfates, molybdates, tungstates and chromates. The anions can be supplied with various counter-ions. Preferred are ammonium, alkali metal and hydrogen (i.e. acid form). The anions can be prepared by the reactive dissolution of various non-anionic materials such as the oxides such as  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{Cr}_2\text{O}_3$ , etc., as well as other materials such as halides, oxyhalides, hydroxyhalides, hydroxides, sulfides, etc., of the metals.

The preferred amount of co-promoter compound present on or deposited on the support or catalyst ranges from 0.1 to 10, preferably from 0.2 to 5 micromoles, expressed as the element, per gram of total catalyst. For purposes of convenience the amount of co-promoter present on the catalyst is expressed as the element irrespective of the form in which it is present.

The co-promoter compounds, salts and/or complexes suitable for use in the preparation of the instant catalysts are compounds, salts and/or complexes which can be solubilized in an appropriate solvent. Preferably, the solvent is a water-containing solvent. More preferably, the solvent is the same solvent used to deposit the silver, alkali metal promoter and rhenium. Preferred co-promoter compounds are the oxyanionic compounds of the co-promoter elements, preferably the ammonium and alkali metal oxyanionates, such as ammonium sulfate, potassium sulfate, cesium chromate, rubidium tungstate, ammonium molybdate, lithium sulfate, sodium tungstate, lithium chromate and the like.

Generally, the carrier is contacted with a silver salt, a silver compound, or a silver complex which has been dissolved in an aqueous solution, so that the carrier is impregnated with said aqueous solution;

thereafter the impregnated carrier is separated from the aqueous solution, e.g., by centrifugation or filtration and then dried. The thus obtained impregnated carrier is heated to reduce the silver to metallic silver. It is conveniently heated to a temperature in the range of from 50 to 600 °C, during a period sufficient to cause reduction of the silver salt, compound or complex to metallic silver and to form a layer of finely divided silver, which is bound to the surface of the carrier, both the exterior and pore surface. Air, or other oxidizing gas, reducing gas, an inert gas or mixtures thereof may be conducted over the carrier during this heating step. Reduction times may generally vary from about 0.5 minute to about 8 hours, depending on the circumstances.

Specific solutions of silver salts with solubilizing and reducing agents may be employed as well, e.g., combinations of the vicinal alkanolamines, alkyldiamines and ammonia. One such example of a solution of silver salts comprises an impregnating solution comprising a silver salt of a carboxylic acid, an organic amine alkaline solubilizing/reducing agent, and an aqueous solvent.

One method of preparing the silver containing catalyst can be found in U.S. Patent 3,702,259. Other methods for preparing the silver-containing catalysts which in addition contain higher alkali metal promoters can be found in U.S. Patent 4,010,115, and U.S. Patent 4,356,312, U.S. patent 3,962,136, and U.S. Patent 4,012,425. Methods for preparing silver-containing catalysts containing higher alkali metal and rhenium promoters can be found in U.S. Patent No. 4,761,394, and methods for silver-containing catalysts containing higher alkali metal and rhenium promoters and a rhenium co-promoters can be found in U.S. Patent No. 4,766,105.

There are known excellent methods of applying the promoters coincidentally with the silver on the carrier. The use of promoter or co-promoter salts which have ions which react with the silver salt in solution is preferably avoided, e.g. the use of cesium chloride together with silver nitrate in an aqueous solution, since then some silver chloride is prematurely precipitated. However, cesium chloride may be used together with a silver salt-amine-complex in aqueous solution, since then the silver chloride is not precipitated prematurely from the solution.

The amount of the alkali metal and/or rare earth and/or rhenium promoters and/or rhenium co-promoters on the porous carrier or catalyst may be regulated within certain limits by washing out the surplus of promoter material with an appropriate solvent, for example, methanol or ethanol.

In general terms, the impregnation process comprises impregnating the support with one or more solutions comprising silver, alkali metal, rare earth, rhenium and rhenium co-promoter. The concentration of the silver (expressed as the metal) in the silver-containing solution will range from 1 g/l up to the solubility limit when a single impregnation is utilized. The concentration of the alkali metal (expressed as the metal) will range from  $1 \times 10^{-3}$  to 12 and preferably from about  $10 \times 10^{-3}$  to 12 g/l when a single impregnation step is utilized. The concentration of the rare earth (expressed as the element) will range from  $1 \times 10^{-4}$  to 1 and preferably from  $5 \times 10^{-4}$  to 0.1 g/l when a single impregnation step is utilized. The concentration of the rhenium (expressed as the metal) will range from  $5 \times 10^{-3}$  to 20 and preferably from  $50 \times 10^{-3}$  to 20 g/l when a single impregnation step is utilized. The concentration of rhenium co-promoter (expressed as the element) will range from about  $1 \times 10^{-3}$  to 20 and preferably from  $10 \times 10^{-3}$  to 20 g/l when a single impregnation step is utilized. Concentrations selected within the above noted ranges will depend upon the pore volume of the catalyst, the final amount desired in the final catalyst and whether the impregnation is single or multiple. Appropriate concentrations can be readily determined by routine experimentation.

The catalysts according to the present invention have been shown to have a particularly high selectivity stability for ethylene oxide production in the direct oxidation of ethylene with molecular oxygen to ethylene oxide. The conditions for carrying out such an oxidation reaction in the presence of the catalysts according to the present invention broadly comprise those already described in the prior art. For purposes of illustration only, the following table shows the range of conditions that are often used in current commercial ethylene oxide reactor units.

TABLE II

*GHSV	1500-10,000
Inlet Pressure	1135-2758 kPa
Inlet Feed	
Ethylene	1-40%
O <sub>2</sub>	3-12%
Ethane	0-3%
Argon and/or methane and/or nitrogen diluent	0.3-20 ppmv total Coolant temperature
chlorohydrocarbon moderator 180-315 °C	
Catalyst temperature	180-325 °C
O <sub>2</sub> conversion level	10-60%
EO Production (Work Rate)	32-256 kg EO/m <sup>3</sup> catalyst/hr.

\*Gas Hourly Space Velocity, volume of gas at standard temperature and pressure passing over volume of packed catalyst per hour.

The invention will be illustrated by the following illustrative embodiments.

#### Illustrative Embodiment 1

This embodiment describes typical preparative techniques for making the catalysts of the instant invention (and comparative catalysts) and the typical technique for measuring the properties of these catalysts.

Part A: Preparation of stock silver oxalate/ethylene-diamine solution for use in catalyst preparation:

- 1) Dissolve 415 grams (g) of reagent-grade sodium hydroxide in 2340 millilitres (ml) deionized water. Adjust the temperature to 50 °C.
- 2) Dissolve 1699 g of "Spectropure" (high purity) silver nitrate in 2100 ml deionized water. Adjust the temperature to 50 °C.
- 3) Add sodium hydroxide solution slowly to silver nitrate solution with stirring while maintaining a temperature of 50 °C. Stir for 15 minutes after addition is complete, and then lower the temperature to 40 °C.
- 4) Insert clean filter wands and withdraw as much water as possible from the precipitate created in step (3) in order to remove sodium and nitrate ions. Measure the conductivity of the water removed and add back as much fresh deionized water as was removed by the filter wands. Stir for 15 minutes at 40 °C. Repeat this process until the conductivity of the water removed is less than 90  $\mu$ mho/cm. Then add back 1500 ml deionized water.
- 5) Add 630 g of high-purity oxalic acid dihydrate in approximately 100g increments. Keep the temperature at 40 °C and stir to mix thoroughly. Add the last portion of oxalic acid dihydrate slowly and monitor pH to ensure that pH does not drop below 7.8.
- 6) Remove as much water from the mixture as possible using clean filter wands in order to form a highly concentrated silver-containing slurry. Cool the silver oxalate slurry to 30 °C.
- 7) Add 699 g of 92 percent weight (%w) ethylenediamine (8% deionized water). Do not allow the temperature to exceed 30 °C during addition.

The above procedure yields a solution containing approximately 27-33%w silver.

Part B: Preparation of impregnation solutions

For Catalyst A (Gd/Re), into a 10 ml beaker is added 0.166 g of (NH<sub>4</sub>)ReO<sub>4</sub> and approximately 2.0 g of ethylene-diamine/H<sub>2</sub>O (50/50 by weight), and the mixture is allowed to dissolve with stirring. 0.079 g of Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O is dissolved in 1 ml of water in a weighing dish, and then added to the perrhenate solution. 0.3416 g of LiNO<sub>3</sub> is dissolved in 2 ml of water and added to the perrhenate solution. The perrhenate/lithium sulfate/lithium nitrate solution is allowed to stir, ensuring complete dissolution. Separately, 0.0839 g of Gd(OAc)<sub>3</sub>·4H<sub>2</sub>O is dissolved in 3 ml of water. Both dopant solutions are then added to 184 g of the above-prepared silver solution (specific gravity = 1.556 g/cc), and the resulting solution is diluted with



water to a total weight of 204 g. One-fourth of this solution is used to prepare a catalyst. 0.0475 g of CsOH is added to a 51 g portion of the silver oxalate/dopant solution to prepare the final impregnation solution.

For Catalyst B (Ce/Re), the procedure for Catalyst A is followed, except that 0.656g of Ce(OAc)<sub>3</sub> is used in place of Gd(OAc)<sub>3</sub>·4H<sub>2</sub>O.

5 For Catalyst C (Yb/Re), the procedure for Catalyst A is followed, except that 0.0873g of Yb(OAc)<sub>3</sub> is used in place of Gd(OAc)<sub>3</sub>·4H<sub>2</sub>O.

For Catalyst D (Re only), the procedure for Catalyst A is followed, except that no Gd(OAc)<sub>3</sub>·4H<sub>2</sub>O is added.

#### 10 Part C: Catalyst impregnation and curing

Catalyst carrier C which is described in Table 1 is a preferred support for the instant invention and is used in the following examples and illustrative embodiments unless otherwise stated.

Approximately 30 g of carrier C are placed under vacuum at 3.33 kPa for 3 minutes at room temperature. Approximately 50 g of doped impregnating solution is then introduced to submerge the carrier, and the vacuum is maintained at 3.33 kPa for an additional 3 minutes. At the end of this time, the vacuum is released, and excess impregnating solution is removed from the carrier by centrifugation for 2 minutes at 500 rpm. If the impregnating solution is prepared without monoethanolamine, then the impregnated carrier is then cured by being continuously shaken in a 8.5 m<sup>3</sup>/hr. air stream flowing across a cross-sectional area of approximately 19.4-32.1 cm<sup>2</sup> at 250-270 °C for 5-6 minutes. If significant monoethanolamine is present in the impregnating solution, then the impregnated carrier is cured by being continuously shaken in a 8.5 m<sup>3</sup>/hr. air stream at 250 °C for 2.5 minutes, followed by a 2.8 m<sup>3</sup>/hr. air stream at 270 °C for 7.5 minutes (all over a cross-section area of approximately 19.4-32.1 cm<sup>2</sup>). The cured catalyst is then ready for testing.

This procedure will yield catalysts on this carrier which contain approximately 13.5%w Ag with the following approximate dopant levels (expressed in parts per million by weight basis the weight of the total catalyst, i.e., ppmw) and which are approximately optimum in cesium for the given silver and rhenium and sulphur levels and support with regard to initial selectivity under the test conditions described below.

	Cs, ppmw	Rare Earth, ppmw	Re, ppmw	S, ppmw
Catalyst A	460	79	280	48
Catalyst B	430	70	280	48
Catalyst C	460	86	280	48
Catalyst D	430	None	280	48

The actual silver content of the catalyst can be determined by any of a number of standard, published procedures. The actual level of rhenium on the catalysts prepared by the above process can be determined by extraction with 20 mM aqueous sodium hydroxide, followed by spectrophotometric determination of the rhenium in the extract. The actual level of rare earth on the catalyst can be determined by standard atomic emission spectroscopy. The actual level of cesium on the catalyst can be determined by employing a stock cesium hydroxide solution, which has been labelled with a radioactive isotope of cesium, in catalyst preparation. The cesium content of the catalyst can then be determined by measuring the radioactivity of the catalyst. Alternatively, the cesium content of the catalyst can be determined by leaching the catalyst with boiling deionized water. In this extraction process cesium, as well as other alkali metals, is measured by extraction from the catalyst by boiling 10 grams of whole catalyst in 20 millilitres of water for 5 minutes, repeating the above two more times, combining the above extractions and determining the amount of alkali metal present by comparison to standard solutions of reference alkali metals using atomic absorption spectroscopy (using Varian Techtron Model 1200 or equivalent). It should be noted that the cesium content of the catalyst as determined by the water leaching technique may be lower than the cesium content of the catalyst as determined by the radiotracer technique.

#### Part D: Standard Microreactor Catalyst Test Conditions/Procedure

3 to 5 grams of crushed catalyst (14-20 mesh) are loaded into a 6.4 mm ( $\frac{1}{4}$  inch) diameter stainless steel U-shaped tube. The U tube is immersed in a molten metal bath (heat medium) and the ends are connected to a gas flow system. The weight of the catalyst used and the inlet gas flow rate are adjusted to achieve a gas hourly space velocity of 3300 ml of gas per ml of catalyst per hour. The inlet gas pressure is 1548 kPa.

The gas mixture passed thorough the catalyst bed (in once-through operation) during the entire test run (including startup) consists of 30% ethylene, 8.5% oxygen, 5% carbon dioxide, 54.5% nitrogen, and 2.0 to 6.0 ppmv ethyl chloride.

The initial reactor (heat medium) temperature is 225 °C. After 1 hour at this initial temperature, the temperature is increased to 235 °C for 1 hour, and then adjusted to 245 °C for 1 hour. The temperature is then adjusted so as to achieve a constant oxygen conversion level of 40%. Performance data at this conversion level are usually obtained when the catalyst has been onstream for a total of at least 2-3 days. Due to slight differences in feed gas composition, gas flow rates, and the calibration of analytical instruments used to determine the feed and product gas compositions, the measured selectivity and activity of a given catalyst may vary slightly from one test run to the next. To allow meaningful comparison of the performance of catalysts tested at different times, all catalysts described in this illustrative embodiment were tested simultaneously with a reference catalyst. All performance data reported in this illustrative embodiment are corrected relative to the average initial performance of the reference catalyst ( $S_{40} = 81.0\%$ ;  $T_{40} = 230^\circ\text{C}$ ).

After obtaining initial performance values for selectivity at 40% conversion the catalysts are subjected to high severity aging conditions. Under these conditions, the catalyst is brought to either 85% conversion or a maximum of 285 °C for a 10-day period to accelerate the aging of the catalyst. After this 10-day aging period, the catalysts are again brought to 40% conversion and reoptimized under standard conditions. The selectivity is again measured, and compared to the original value of the fresh catalyst. After the new selectivity value is determined, this cycle is repeated, and the selectivity decline of the catalyst is continuously measured under standard 40% conversion conditions in 10-day cycles relative to its fresh initial performance. The results are presented below in Table III. All selectivity values are expressed as %. The initial performances of Catalysts A, B, C and D were determined to be the same, within experimental error. Initial  $S_{40}$  values of  $86.0\% \pm 0.4\%$  and  $T_{40}$  values of  $260^\circ\text{C} \pm 3^\circ\text{C}$  were obtained.

Loss of Selectivity (%) = {  $S_{40}$ , % (Fresh) } - {  $S_{40}$ , % (Aged) }

TABLE III

Loss of Selectivity from Fresh Catalyst Total Days at Either 85% Conversion or 285 °C (Data Obtained at 40% Conversion Conditions)					
Catalyst	10 Days	20 Days	30 Days	40 Days	50 Days
A (Re/Gd)	0%	0.8%	1.4%	2.2%	3.4%
B (Re/Ce)	0%	0%	0.4%	--	--
C (Re/Yb)	0%	--	--	--	--
D (Re)	1.2%	2.3%	3.4%	5.0%	6.1%

As mentioned previously, selectivity decline is of tremendous economic importance when choosing a catalyst, and retarding this decline rate can lead to significant savings in costs. As can be seen from Table III, Catalyst D, which does not contain a rare earth element in combination with Re, decreases in selectivity much more rapidly than do the catalysts which contain a rare earth element. Catalysts which contain rare earth elements in combination with rhenium maintain their selectivity significantly longer than catalysts without added rare earth elements and are thus significantly advantaged.

#### Claims

1. An ethylene oxide catalyst for the vapour phase production of ethylene oxide from ethylene and oxygen comprising a catalytically effective amount of silver, a promoting amount of alkali metal, a promoting amount of a rare earth metal compound and a promoting amount of rhenium supported on a suitable support.
2. A catalyst according to claim 1, characterized in that it also comprises a rhenium co-promoter, selected from the group of sulphur, molybdenum, tungsten, chromium or mixtures thereof.
3. A catalyst according to claim 1 or 2, characterized in that the amounts of the components, based on the total catalyst, are in the ranges of:

- silver, from 1 to 30 wt%,
  - alkali metal promoter, expressed as the metal, from 10 to 1500 parts per million by weight,
  - rare earth promoter, expressed as the element, from 10 to 1000 parts per million by weight,
  - rhenium promoter, expressed as the metal, from 19 to 1860 parts per million by weight (from 0.1 to 10 micromoles per gram),
  - optional rhenium co-promoter, from 0.1 to 10 micromoles per gram;
- and the surface area of the support is in the range of from 0.05 to 10 m<sup>2</sup>/g.

4. A catalyst according to any one of claims 1 to 3, characterized in that the alkali metal promoter and/or the rare earth metal and/or the rhenium promoter and/or the the rhenium co-promoter is present in the form of an oxide or an oxygen-bound species.

5. A catalyst according to any one of claims 1 to 4, characterized in that the alkali metal is selected from the group of potassium, rubidium, cesium, lithium and mixtures thereof.

6. A catalyst according to any one of claims 1 to 5, characterized in that the rare earth metal is selected from the group of cerium, neodymium, samarium, gadolinium, dysprosium, erbium, ytterbium and mixtures thereof.

7. A catalyst according to claim 6, characterized in that the rare earth metal is selected from the group of cerium, gadolinium, ytterbium and mixtures thereof.

8. A process for preparing a catalyst according to any one of claims 1 to 7, which comprises impregnating a porous refractory support with one or more solutions comprising silver, alkali metal, rare earth metal compound, rhenium and optionally rhenium co-promoter, wherein the concentration (expressed as the element) in the solution(s) ranges are between:

- 1 gram/litre and the solubility limit of the silver,
- $1 \times 10^{-3}$  and 12 grams/litre of the alkali metal,
- $1 \times 10^{-4}$  and 1 gram/litre of the rare earth,
- $5 \times 10^{-3}$  and 20 grams/litre of the rhenium, and
- $1 \times 10^{-3}$  and 20 grams/litre of the optional rhenium co-promoter,

to provide the catalyst with a catalytically effective amount of silver, a promoting amount of alkali metal, a promoting amount of rare earth metal compound, a promoting amount of rhenium and optionally a promoting amount of rhenium co-promoter.

9. A process according to claim 8, characterized in that after impregnation, the silver is reduced to metallic silver by heating at a temperature between about 50 °C and about 600 °C.

10. Use of a catalyst according to any one of claims 1 to 7 in a process for the vapour phase production of ethylene oxide from ethylene and oxygen.



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 94 20 1334

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
D,Y	EP-A-0 266 015 (SHELL) * page 2, line 26 - line 40 * * page 3, line 6 - line 24 * * claims *	1-10	B01J23/68 C07D301/10
Y	GB-A-1 371 685 (TORAY IND.) * page 1, line 13 - line 66 * * claims *	1-10	
D,A	EP-A-0 011 356 (TORAY)		
A	EP-A-0 496 470 (SHELL)		
A	EP-A-0 480 537 (UNION CARBIDE)		
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			B01J C07C C07D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 August 1994	Examiner Lo Conte, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document	